



## Outlays on R & D Programmes of CSIR during Fourth Five-Year Plan

The plan and non-plan outlays on R & D programmes of the Council of Scientific & Industrial Research (CSIR) during the Fourth Five-Year Plan (1969-74) are Rs 50.00 crores and Rs 71.12 crores respectively according to the final report of the Planning Commission. Thus, the total outlay for CSIR for the current plan shows an increase of about 108% over the Third Plan figure (Rs 58.38 crores) (Table 1). Considering the total Fourth Plan allocation of Rs 338.58 crores for scientific research under CSIR, Atomic Energy Commission and the Ministry of Education's Surveys, etc., the Council's share works out to about 36%.

Broad guidelines for streamlining the national research effort have been provided in the report. The plan also draws attention to some of the basic lacunae in the programmes and policies followed so far and the imbalances in the spending on R & D in certain sectors. Two typical sectors cited, to which adequate attention has not been paid despite their being of vital significance to the growth of science and technology leading to economic growth, are the development of natural resources and training of scientific and technical manpower of high quality. One of the possible reasons suggested

for the imbalanced growth is the lack of a central authority to study and decide *inter se* allocation in various areas of scientific and technological activities.

With respect to the proposals concerning the programmes of CSIR, satisfaction is expressed over the recent trend of paying greater attention to purposeful research and development programmes, especially those which could be completed within the Fourth Plan period. A Working Group comprising nine expert committees has identified priority projects relating to technologies for special glass and ceramics, non-ferrous metals like magnesium, special batteries required by defence, high polymers and synthetic fibres, biochemicals, and materials for electronic industries such as pure silicon, synthetic quartz crystals, and special classes of ferrites. Food research, grain storage structures, mining and mineral beneficiation, tropicalization, welding technology and design of microwave towers, reactor pressure vessels, and development of antifertility agents are among the other important subjects indicated as deserving priority. A central machinery set up under the chairmanship of the Member (Industry), Planning Commission, for providing guidelines to CSIR laboratories identified three priority areas: steel, has chemicals and instruments; subgroups are engaged in identifying important problems for research and development in these areas.

Specific proposals are made in regard to the translation and scaling up of the laboratory and pilot plant scale results to industrial scale. It is laid down that while the laboratories will provide experimental and

pilot plant data to entrepreneurs, consulting engineering firms should be entrusted with the work of design engineering and feasibility studies. In special cases design cells may be set up in the laboratories themselves or for groups of laboratories in the same field. It is recommended that where the integration of several disciplines is required, more than one CSIR laboratory in association with industry and outside agencies should cooperate on selected projects.

Pointed attention is drawn to the need for avoiding duplication of research work in the CSIR laboratories as well as between CSIR laboratories and the laboratories of other central agencies. To avoid overlapping of research, the need for a detailed examination of the projects proposed by the regional laboratories is stressed. The need to review such projects of the national laboratories as have been in hand for quite some time is indicated. A review of the working of the field stations has been suggested with a view to rationalizing their work and making them more effective.

With regard to the industrial exploitation of the results of research, it is suggested that the National Research Development Corporation of India should lay greater stress on its development activity and set up prototype or pilot plants in collaboration with industry or on its own. It is recommended that the Corporation will select from the laboratory processes, those that are promising for upscaling and carry out techno-economic evaluation of such processes with the assistance of industrial consultants. A sum of Rs 2 crores has been earmarked as enterprise capital to be spent on establishing the feasibility of processes. Among the projects proposed to be taken up for such studies in association with industrial consultants are those on silicon carbide and lindane.

Table 1—Outlays on R & D Programmes of CSIR during Third and Fourth Plans

(Figures in Rs crores)

	PLAN	NON-PLAN	TOTAL
Third Plan	33.04	25.34	58.38
Fourth Plan	50.00	71.12	121.12



## Evaluation and Development of Indigenous Clays for Petroleum Industry: IIP's Work

Clays are mainly used in petroleum industry for the finishing of the lube stocks, treatment of light aromatic extracts, pre-treatment of catalytic reformed feedstocks for removing trace impurities, deodorizing of solvents and re-refining of used lubricating oils. Clays for these purposes may be natural or activated; the latter are nearly two to three times more costly and possess greater activity.

### Lube finishing

Clay treatment has been extensively used as a finishing step for lube stocks passing through bleaching, clarifying, dehydrating and neutralizing processes. Adsorbent clays decolorize the oil by separating solid, suspended, colloidal and dissolved impurities such as finely divided and colloidal carbon, complex tarry compounds of high molecular weight, and dissolved colouring matter. After clay contacting, the oil exhibits higher interfacial tension, decreased acidity, decreased sulphur, nitrogen and oxygen content, greater colour and oxidation stability.

At the request of the Indian Oil Corporation Ltd, the Indian Institute of Petroleum (IIP), Dehra Dun undertook studies to find out a suitable indigenous clay for the clay contacting unit of the Barauni lube plant. The important performance characteristics of various indigenous and imported clays, such as bleaching efficiency, filterability, oil retention, colour stability and settling were determined. Contacting temperature, time of contact, amount of clay, mode of agitation were the main process variables chosen with respect to the activity of the clay and the nature of the oil, and accordingly optimum conditions were determined.

The investigation led to the selection of an indigenous clay having efficiency equivalent to that of some of the best imported clays for the lube plant at the Barauni Refinery which has a production capacity of 46 000 tonnes of lubricants and requires about 2500 tonnes of clay per annum, thus saving foreign exchange to the tune of Rs 10-12 lakhs per annum. At present the purchase of the clays

at the Barauni Refinery is being made on the recommendations based on the evaluation and performance studies conducted at IIP.

### Re-refining of used lubricating oils

The lubricating oils presently produced in the country are far short of their demand, and annually as much as Rs 30 crores worth of lubricants are being imported. A process has been developed by IIP to re-refine used lubricating oils as a measure to save foreign exchange spent on the import of fresh lubricants. By this process, used lubricants are re-refined and additive-treated so as to impart the original characteristics. The re-refining process includes treatment with clays. Besides improving the colour and odour, the purpose of the clay treatment is to bring down the level of impurities and acidity. In some cases, when acidity is high, sodium carbonate is added along with the clay in order to effect complete neutralization. The clay treatment substantially enhances the oxidation stability of the oil. The action of clay in re-refining is specific and hence the optimum conditions for the best results are to be worked out in the laboratory.

Evaluation studies were carried out for the selection of an efficient indigenous clay for re-refining used oils. Some of the indigenous clays were found to have the same efficiency as that of the imported ones. The present estimate of used lubricating oils available for re-refining is about 60 000 tonnes, and about 4000 tonnes of clay are required for treatment. If the entire requirements of this clay are met indigenously, foreign exchange worth about Rs 20 lakhs per year can be saved.

Presently, a total capacity of about 2000 tonnes per year of re-refining plants has been licensed to industry by the institute using the know-how developed and some of them are already under erection. The present utilization of clays in the plants thus comes to about 140 tonnes costing about Rs 70 000 worth of foreign exchange per year.

### Treatment of light aromatic extracts

Removal of trace quantities of olefins and diolefins is necessary if high purity aromatics, viz. benzene, toluene and xylenes, are to be obtained from re-formed aromatic stocks. The clay polymerizes trace contaminants of olefins and diolefins in the raw extract stream which are easily removed in subsequent distillation, thus producing aromatics of nitration grade.

At the instance of the Gujarat Refinery, IIP undertook a study for finding a suitable indigenous clay, which could be satisfactorily used in the clay percolation unit of the Udex plant of the refinery. The first charge of the clay as well as one refill was imported. Investigations were carried out at IIP on thirteen indigenous and five imported clays. The preliminary screening of the clays was done on Filtrol type apparatus fabricated at IIP; and finally, seven effective clays were selected for detailed investigation. These were evaluated in continuous runs for five days for each clay at specified temperature, pressure and space velocity under simulated plant conditions using an actual Udex extract and employing a fixed bed of clay. During each 24-hr period of the five-day run, the percolate collected was fractionated into benzene, toluene and xylene cuts, and acid wash colour test and bromine index were determined for each cut.

On the basis of the study, some indigenous clays were found to possess performance characteristics which were as good as those of the imported reference clay. This will result in a recurring saving of foreign exchange equivalent to about Rs 1 lakh per annum.

### CGCRI Develops Cheaper Dinnerware and Insulator Bodies

At the instance of a pottery manufacturing firm in Calcutta the Central Glass & Ceramic Research Institute (CGCRI), Calcutta developed earthenware bodies maturing at cone 9 (1285°C) suitable for making dinnerware and low- and high-tension insulators using entirely indigenous raw materials. The firm had been using so far imported ball clay and china clay for making these ceramic



bodies. The green modulus of rupture, fired colour, water absorption and workability of the earthenware body were found to be comparable to those of the bodies hitherto used, while the green mechanical strength of the new body was even better. This body is now under regular commercial production. The insulator body, also characterized by good vitrification, high fired modulus of rupture and good workability has been put to regular commercial use by the firm who are manufacturing low-tension and high-tension insulators satisfactorily.

This development has led to substantial import substitution worth more than Rs 25 lakhs and sizeable reduction in the cost of production.

### Benzonitrile from Toluene: CFRI's Process

A process for the production of benzonitrile from surplus toluene available in the country as a result of increased coal carbonization capacity in steel plants and coke ovens has been developed by the Central Fuel Research Institute (CFRI), Dhanbad.

Benzonitrile is an important intermediate, capable of undergoing addition and substitution reactions to yield a variety of organic compounds. Benzonitrile can be hydrolysed to yield sodium benzoate needed by the food preservation industry, or to benzoic acid in demand in the pharmaceutical, plastic, dyestuffs and other industries. Partial

The costs of dinnerware and insulator bodies developed at the institute are lower by about Rs 40 and Rs 65 per tonne respectively as compared to those of the standard bodies hitherto used by the firm, resulting in a net saving of about Rs 12 lakhs per annum on the basis of the present slip house turn-over. The overall saving would be still more due to reduction in breakages at different stages of production, reduction in firing temperature and improvement in the quality of finished products and substitution of quartz stone by silica sand in the body composition. The total body manufacturing capacity of the insulator factory has also been increased by substitution of silica sand in place of quartz stone.

reduction of benzonitrile followed by hydrolysis yields benzaldehyde required for cosmetics, perfumeries, and medicinal purposes. Benzonitrile and its derivatives also constitute important basic raw materials in the production of triphenyltriazine, benzoguanamine resins and solvents.

Introduction of the nitrile group into aromatic molecules is a laborious process and normally involves a series of reactions such as halogenation or sulphonation followed by reaction with sodium cyanide or conversion to the amine followed by diazotization and coupling with cuprous cyanide, or alternatively oxidation to the corresponding carboxylic acid fol-

lowed by conversion to the amide and dehydration to the nitrile.

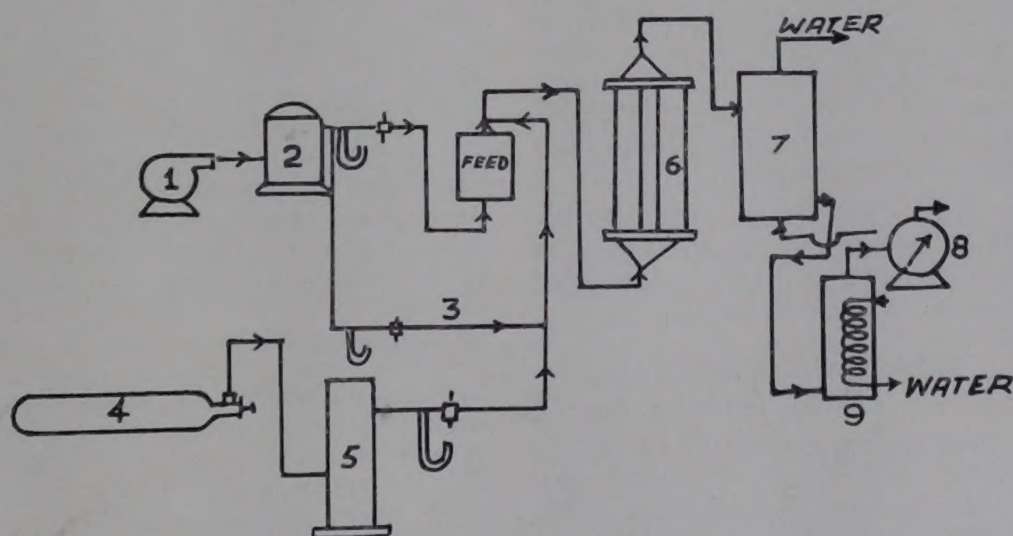
The process developed by CFRI (under patent) dispenses with the use of expensive chemicals and yields a pure product on a continuous basis. The institute has also developed a specific catalyst for the process which employs catalytic vapour phase oxidative ammonolysis of toluene with air and ammonia at atmospheric pressure. The reaction products are collected in three sets of condensers, the first cooled with air, the second with circulating water at 10°C, and the third under crushed ice. The major part of the nitrile is trapped in the air condensers, the ice-cooled traps holding the residual nitrile along with traces of the unreacted toluene. Toluene is isolated from the outgoing stream by refrigeration, effecting near quantitative recovery. The yield of benzonitrile obtained (per pass) is 60 kg per 100 kg of toluene charge. With the recycling of the unreacted feedstock, the yield is higher.

### Commercialization of CFRI Processes

The Central Fuel Research Institute (CFRI), Dhanbad has signed on behalf of CSIR a development contract with the Chemical and Metallurgical Design Company (P) Ltd (CHEM METAL), New Delhi for the commercial exploitation of the CFRI processes for the production of 3- and 4-cyanopyridines, benzoic acid and benzaldehyde, used in pharmaceutical and food preservation industries. CHEM METAL will undertake design and engineering of the plants and supply turn-key plants to entrepreneurs.

CFRI processes use beta-picoline for 3-cyanopyridine, gamma-picoline for 4-cyanopyridine and toluene for benzoic acid and benzaldehyde production, the raw materials for the processes being the byproducts of coal carbonization. The technique employed in all cases is the catalytic vapour phase conversion of the materials to corresponding finished products employing catalysts also developed at the institute.

In the case of cyanopyridines, the bases are simultaneously reacted with air and ammonia, while in the other



Flow diagram for the production of benzonitrile from toluene: 1. Air blower, 2. Surcharge tank, 3. Secondary air, 4. Ammonia cylinder, 5. Ammonia surcharge tank, 6. Reactor, 7. Condenser, 8. Gas meter, 9. Water cooler



two cases air or air enriched with oxygen is used. The processes give pure products in good yield and dispense with expensive oxidizing agents, hitherto being used. Another distinguishing feature of the processes is that they are continuous.

### Polymerization of Polar Monomers using Vanadium based Ziegler-Natta Catalysts

Work on the polymerization of polar monomers using vanadium halides and organometallic compounds is scanty, and the mechanism of polymerization is not well understood. Hence, a systematic study of the use of Ziegler-Natta catalyst systems based on vanadium halides for the polymerization of polar monomers like methyl methacrylate and acrylonitrile was carried out by Shri S. S. Dixit of the National Chemical Laboratory, Poona, under the guidance of Dr S. L. Kapur. A comparative study of styrene, a non-polar monomer, was also made.

To study the effect of the medium on the catalyst preparation, *n*-hexane was replaced by a polar medium like acetonitrile, and monomers like acrylonitrile and methyl methacrylate were polymerized. A detailed kinetic study was made with respect to the effect of catalyst ratio, effect of monomer and catalyst concentrations on the rate of polymerization and molecular weights to determine the order of the reaction with respect to the monomer and catalyst. Overall activation energy was determined from the effect of temperatures on the rate of polymerization in order to understand the mechanism of Ziegler-Natta polymerization.

For a better understanding of the reaction mechanism, the effect of added reagents such as zinc diethyl hydroquinone, 1,1-diphenyl picryl hydrazyl, triethylamine, pyridine and diethyl ether during polymerization was also studied. The valence of vanadium in the  $\text{VCl}_4\text{-Al}$  alkyls catalyst systems was also determined to understand the nature of the catalytic species. The Langmuir-Hinshelwood mechanism was used to explain the observations made regarding the maximum conversion at a particular ratio of combination of the catalysts. The order of the reactions with respect to catalyst and monomer concentrations was

determined for each catalyst system, and rate constants were calculated.

Polymethyl methacrylate obtained with  $\text{VOCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$  and  $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$  in *n*-hexane showed the presence of stereoblock structure which was determined from NMR spectra. Polymethyl methacrylate obtained with  $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$  in acetonitrile showed the presence of heterotactic structure.

When basic additives were added to  $\text{VOCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$  catalyst system, the rate of polymerization and molecular weights increased tremendously. Syndiotacticity also increased in the order of triethyl amine > diethyl ether, whereas pyridine had no effect on the stereoblock structure of polymethyl methacrylate. The increase in syndiotacticity has been attributed to adduct formation of electron donor with the aluminium alkyl, and hence the change in the structure of polymers. The effect of zinc diethyl in decreasing the molecular weight and also rate of polymerization due to chain transfer of styrene and methyl methacrylate suggested a coordinate anionic mechanism.

The structures of polymers were characterized by IR and NMR spectra measurements. From NMR studies, mechanisms of polymerizations with different catalyst systems for various monomers studied were deduced as coordinated anionic and in some cases both radical and anionic mechanisms operated simultaneously.

The present investigation has established the mechanism of polymerization for the polar monomers, which can be effectively polymerized at room temperature using the vanadium based Ziegler-Natta catalysts. This was hitherto not possible with the conventional Ziegler-Natta catalyst based on titanium.

Shri Dixit was awarded the Ph.D. degree by the University of Bombay (1970) for his thesis entitled 'Studies in polymerization'.

### Pollen Grains of Some Indian Thalamiflorae

Morphological researches in angiosperms have been mainly concerned with the determination of the primitive and advanced taxa of plants. Thalamiflorae comprise Ranalian families which by and large are

supposed to be the most primitive in dicotyledons.

A study of the pollen grains of Thalamiflorae has been made by Shri Hafiz Ahmed Khan of the National Botanic Gardens (NBG), Lucknow, under the guidance of Dr P. K. K. Nair of NBG and Dr Mohd Farook of the Aligarh Muslim University, Aligarh.

The study has been mainly aimed at correlating the palynological data with other available knowledge on the morphology of some families comprising the Thalamiflorae. Relevant information from the literature on embryology, cytology and other botanical disciplines along with the pollen morphology has been drawn in interpreting the relationship of the various families described. An attempt has been made to throw light on the origin and the possible lines of evolution in Thalamiflorae on the basis of pollen grains.

Pollen grains of Indian Ranunculaceae, Nymphaeaceae, Magnoliaceae, Annonaceae and Menispermaceae have been studied in detail. In addition, pollen morphology of 54 genera of various other Thalamiflorae has been studied.

### Ranunculaceae

Considering the family as a whole the pollen grains are pantoporate in *Clematis grata*, *Thalictrum* sp., *Caltha palustris* (var. *alba*), and *Ranunculus arvensis*, 3-zonocolporate with a faint endocolpium in *Paeonia* and 3-zonocolpate in other taxa. Pollen morphological differences within the species are quite significant in *Clematis* and *Ranunculus*. The organization of pollen is of very simple type with weakly defined apertures and faint surface patterns except for *Ranunculus arvensis* which has heavily ornamented exine. The pantoporate sporomorphs of *R. arvensis* and other taxa have their parallel in the primitive families of monocots (e.g. Alismataceae; Alisma).

### Nymphaeaceae

Specific differences in pollen have been observed with regard to *Nymphaea*. The presence of monocolpate pollen grains in the family is an indication of its affinity with the monocots as well as with other families of Ranales. Its probable relationship with the Ranunculaceae



is evidenced by the presence of 3-colpate pollen grains in *Nelumbo*, *Vallisneria* and *Euryale*.

### Magnoliaceae

Schisandra and other related members are different from Magnolia type. Microspores (pollen grains) are formed in tetrads and remain enclosed within the wall of the mother cell—a unique type for the dicot. Pollen morphology agrees with the sum total of the other morphological characters that make Illiciaceae, Winteraceae and Trochodendraceae different from Magnoliaceae in a somewhat restricted sense. It appears that Magnoliaceae has evolved along a line independent of the other closely related families.

### Annonaceae

The pollen grains are very delicate and often affected by chemical treatment involving acetolysis and as such these grains were treated with 70% alcohol and stained with safranin before mounting in glycerin jelly. Pollen grains are monocolpate inaperturate in *Asimina* sp. and the exine surface is either foveolate or granulose. The exine strata are not clearly differentiated. The affinities of the family with Magnoliaceae, Myristicaceae, Lauraceae and Monimiaceae are evidenced in pollen morphology.

### Menispermaceae

Pollen grains are 3-zonocolporate and are relatively smaller than those in other Ranales. The exine surface is either areolate or granulose. *Cissampelos pareira* which varies in its external gross morphology has pollen grains of variable ornamentation (reticulation of variable types). An expression of the geographical distribution of plants is evident from the pollen morphology of this genus which shows a possible inclusion of several Biotypes in the genus. In *Tinospora cordifolia* differences in apertural forms have been noted in the material collected from two different localities. Menispermaceae appear to be more closely related to Ranunculaceae than to Magnoliaceae.

An analysis of the apertural morphoforms in different families of Thalamiflorae has been made. All the apertural morphoforms of pollen

grains found within the angiosperms are met within the Thalamiflorae alone and even in some of its eury-palynous families, viz. Malvaceae and Ranunculaceae. It may therefore be presumed that there are various lines of evolutions from the fundamental 3-colpate Ranalian stock, while on the monocolpate Magnolian stock there is linear

evolution as all the families on the stock are monocolpate except for minor deviations.

The researcher Shri Hafiz Ahmed Khan was awarded the Ph.D. degree of the Aligarh Muslim University (1969) for his thesis entitled, 'Pollen grains of some Indian Thalamiflorae.'

## PROGRESS REPORTS

### CLRI Annual Report: 1968

The research programmes of the Central Leather Research Institute (CLRI), Madras were worked out under 48 main projects during the year 1968 according to its annual report published recently. Eight schemes were financed by other organizations such as the U.S. Department of Agriculture under PL 480 funds, the Indian Council of Agricultural Research, the National Research Development Corporation of India, and USAID agencies. Outlining the significant results of research and important events during the year in the first two sections respectively, the 72-page report records the research progress in the six main areas: (1) Raw hides and skins and related byproducts, (2) Collagen, (3) Tanning agents and mechanism of tannages, (4) Tanning and finishing processes, (5) Leather auxiliaries, and (6) Footwear and leather goods.

A new series of copolymeric emulsions using acrylic monomers and natural resins like shellac have been developed. Good and cheap substitutes for the conventional auxiliary agents, the emulsions are stable, give highly water-resistant films with good adhesion and improved gloss and possess a wide range of applications from finishing of soft materials like leather to rigid surfaces as in wall finishes. A filler from lac resin has been developed for improving the quality of full chrome and semi-chrome suedes. The filler imparts tightness to the nap, fills up the loose and thin ends, improves buffing characteristics and increases the fullness and handle of suede leathers. An anionic resin based on urea and formaldehyde, developed by CLRI, is very stable and easy to apply as a retanning agent; the resin has given good results with Indian raw hides

and skins. The institute has also developed a cationic retanning and dyeing agent using the same raw materials.

A supple leather developed by CLRI for use in a pneumatic door closer replaces the presently used devices based on hydraulics. The product has been successfully utilized by a local manufacturer of door-closers in place of imported washers.

An important achievement of the institute during the year under report is the development of a process for the manufacture of shrunken grain leathers from blue chrome leathers. The process can be applied to any chrome tanned stock in shrunken pattern and enables the utilization of non-exportable chrome blue tanned skins. The manufacture of high closed shoes, watch and sandal straps and other leather goods of quality from cow hides has been made possible by a process developed by the institute. In this process, cow hides of medium range are cut into crops and bellies in raw condition, the crops are tanned into full chrome and chrome retan upper leather, and the bellies are tanned into retan uppers and linings. Turtle flipper, a byproduct of the meat industry, has been used for the production of leathers for manufacturing fancy goods which have great export potential. Methods for tanning and finishing of these skins with good gloss using lacquer have also been worked out.

Discolouration of large quantities of pig bristles and other keratinous fibres results in downgrading the fibres. Investigations at CLRI have shown that the keratinous fibres could be made to regain the attractive jet black lustrous shades by scouring and mordanting using pyrogallol tannin with metallic strikers.



Of specific interest to sports goods industry are: (i) a soft leather suitable for the manufacture of leather gloves used for wicket keepers in cricket, and (ii) leathers suitable for manufacturing cricket and hockey balls. The institute worked out processes for these leathers.

One of the projects of basic nature was concerned with the modification of collagen with a view to producing leathers with improved properties. Under this project collagen was successfully grafted with vinyl monomers (up to 160%) using

ceric ion redox system with a view to combining the properties of the natural polymer with those of the synthetic polymers. The grafted pelts are fuller, more uniform and hold out the possibility of making leathers with improved properties.

Eighty research papers were published during the year. Thirty-one processes developed by CLRI were released to industry during the year. The value of goods supplied to consumers from the pilot plants of the institute amounted to Rs 1 93 000.

## CSIR SUPPORT TO RESEARCH

### Completed Schemes

#### Transformations of Terpene Hydrochlorides

In a CSIR research scheme functioning at the Department of Chemistry, Christian Medical College, Vellore, studies on the transformations of terpene hydrochlorides have been carried out by the research fellow Shri N. V. Muraleedharan working under the direction of Prof. James Verghese of the Department.

Terpene hydrochlorides serve as raw materials for obtaining innumerable derivatives of the *p*- and *m*-menthadiene series. The studies under the scheme were carried out in three phases: (i) chemistry of hydrolysis and dehydrohalogenation of dipentene dihydrochloride; (ii) dehydrohalogenation of  $\alpha$ -terpinene dihydrochloride; and (iii) chemistry of *m*-menthadienes derived from (+)-sylvestrene and carvestrene dihydrochlorides and the interrelationship of the dihydrohalides.

#### Dipentene dihydrochloride

The chemistry of the hydrolysis and dehydrohalogenation of dipentene dihydrochloride (1,8-dichloro-*p*-menthane) has received considerable attention. Earlier literature refers mostly to qualitative studies. For complete decomposition of dipentene dihydrochloride, it was found necessary to agitate vigorously the halogen derivative with 2% KOH at 90° for 5 hr. The major product of hydrolysis is *dl*- $\alpha$ -terpineol with minor quantities of its isomers, *cis*- and *trans*-terpins, dipentene and terpinolene.

Previously, the expulsion of HCl from dipentene dihydrochloride by interaction with aniline was reported to yield mainly dipentene, with unspecified amounts of terpinolene and  $\alpha$ -terpinene. No quantitative data are available on these *p*-menthadienes. The precise fractionation of the dehydrohalogenated oil followed by conventional chemical analysis of the several cuts indicated the presence of dipentene and terpinolene. However, the GLC analyses of the oil clearly showed the presence of dipentene (64.1%), terpinolene (23.9%),  $\alpha$ -terpinene (1.4%) and  $\gamma$ -terpinene (1.7%).

#### $\alpha$ -Terpinene dihydrochloride

Only a few dehydrohalogenation studies have been made on  $\alpha$ -terpinene dihydrochloride. Earliest report on the decomposition of this dihydrochloride by stirring with 2% aq KOH at 100° for 15 hr cites 'rather pure terpinene' as the sole isolated hydrocarbon in addition to terpinenols. Using aniline, the dehydrohalogenation provided  $\alpha$ -terpinene,  $\gamma$ -terpinene and terpinolene.

$\alpha$ -Terpinene dihydrochloride on dehydrohalogenation with 2% aq KOH yields  $\alpha$ -terpinene (48.10%),  $\gamma$ -terpinene (35.62%), terpinolene (16.25%) and unidentified hydrocarbons ( $>0.03\%$ ); and with aniline yields  $\alpha$ -terpinene (31.2%),  $\gamma$ -terpinene (33.1%), terpinolene (23.6%),  $\alpha$ -phellandrene (2.7%),  $\beta$ -phellandrene (0.8%), dipentene (2.3%), 2,4(8)-*p*-menthadiene (1.9%) and *p*-cymene (3.7%).

#### *m*-Menthadiene from sylvestrenes

From the *m*-menthadienes obtained by processing sylvestrene dihydro-

chloride with aniline, by precise fractionation, pure (GLC) sylvesterpilolene was isolated for the first time in 1.91% yield. In Wallach's test, this hydrocarbon gave an intense methylene blue colour.

With the aid of infrared, ultraviolet and nuclear magnetic resonance spectroscopy, the structure of sylvesterpilolene was deduced as *m*-mentha-1(2), 3(8)-diene.

The reactions of sylvesterpilolene investigated were: (i) hydrohalogenation, (ii) action of maleic anhydride, (iii) action of 20% aq phosphoric acid, and (iv) disproportionation.

With hydrogen halide, sylvesterpilolene afforded carvestrene dihydrohalide.

In agreement with the structure of sylvesterpilolene, the hydrocarbon absorbed maleic anhydride quantitatively and yielded an adduct, mp 306-308° (decomp.); the conditions for the adduction were standardized.

Further, the action of 20% aq phosphoric acid revealed that sylvesterpilolene is highly resistant to isomerization; over 85% of the hydrocarbon remained unchanged. By comparative GLC, isosylvesterpilolene was detected as a minor constituent of the isomerisate.

Under the influence of palladized charcoal, sylvesterpilolene underwent, in the main, a disproportionation satisfying the following equation:  $3C_{10}H_{16}$  (sylvesterpilolene)  $\rightarrow 2C_{10}H_{14}$  (*m*-cymene) +  $C_{10}H_{20}$  [*m*-menthane (s)].

Another new hydrocarbon trapped from the *m*-menthadienes was isosylvesterpilolene. For this purpose, the isosylvesterpilolene-sylvesterpilolene portion of the dehydrohalogenate, bp 87-88°/20 mm, was relieved of sylvesterpilolene by adduction with maleic anhydride; the oil recovered was 94% pure (GLC) isosylvesterpilolene. This oil afforded a new optically inactive tetrabromide, mp 127-128° (decomp.). NMR data showed that the sample of isosylvesterpilolene and its tetrabromide were respectively *m*-mentha-1(6), 3(8)-diene and 1,6,3,8-tetrabromo-*m*-menthane. Debromination of the tetrabromide with zinc dust in alcohol-ether medium released pure (GLC) isosylvesterpilolene in 87.29% yield (theor.). To Wallach's reagents, isosylvesterpilolene responded



just like isosylvesterpino-  
lene. The structural re-evaluation of the pure  
isoveterpinolene through NMR  
spectroscopy further confirmed it  
to be *m*-mentha-1(6), 3(8)-diene.

On hydrochlorination and hydro-  
bromination, isosylvesterpino-  
lene gave carvestrene dihydrochloride and  
carvestrene dihydrobromide respec-  
tively.

### Carvestrene dihydrohalides

The preparation of carvestrene  
dihydrochloride from sylveterpino-  
lene, isosylvesterpino-  
lene and also  
from their mixtures (bp 87-88°/20 mm)  
derived from sylvestrene dihydro-  
chloride has been studied. Of these,  
the last raw material is the most  
convenient source for preparing the  
dihydrochloride.

A comparison of the IR and  
NMR spectra of carvestrene and  
sylvestrene dihydrochlorides showed  
that they are identical; this substan-  
tiated the original finding based on  
mixed melting point that carvestrene  
dihydrochloride is the racemate of  
sylvestrene dihydrochloride.

Likewise, the infrared spectral  
features of sylvestrene dihydro-  
bromide and carvestrene dihydro-  
bromide suggested that the latter is  
( $\pm$ )-sylvestrene dihydrobromide.

Resolution of the *m*-menthadi-  
enes generated from carvestrene di-  
hydrochloride on Silicone Rubber  
column indicated the presence of  
four components of which three were  
identified as ( $\pm$ )-sylvestrene, iso-  
sylvesterpino-  
lene and sylveterpino-  
lene.

Precise fractionation of the de-  
hydrohalogenate from carvestrene  
dihydrochloride gave two cuts: (i)  
bp 74-85°/20 mm, and (ii) 85-88°/20  
mm. Cut (i) furnished another  
optically inactive tetrabromide, mp  
123.5°. From cut (ii) isosylvesterpino-  
lene tetrabromide and sylveterpino-  
lene-maleic anhydride adduct  
were available and this further con-  
firmed that isosylvesterpino-  
lene and sylveterpino-  
lene were components  
of the oil. Through NMR spectro-  
scopy, the inactive tetrabromide was  
proved to be 1,6,8,9-tetrabromo-*m*-  
menthane. The concurrence of the  
NMR and IR spectra of the tetra-  
bromide with those of (+)-sylves-  
trene tetrabromide clearly established  
the fact that the derivative under

consideration is ( $\pm$ )-sylvestrene tetra-  
bromide.

Debromination of ( $\pm$ )-sylvestrene  
tetrabromide with zinc dust in  
alcohol-ether medium gave pure  
(GLC) ( $\pm$ )-sylvestrene, viz. *m*-men-  
tha-1(6), 8(9)-diene. Moreover, the  
complete identity of the NMR and  
IR spectra of this hydrocarbon with  
that of (+)-sylvestrene confirmed that  
the *m*-menthadiene released from  
( $\pm$ )-1,6,8,9-tetrabromo-*m*-menthane  
is ( $\pm$ )-sylvestrene. The optically in-  
active *m*-menthadiene did not re-  
spond to Wallach's reagents.

Refluxing carvestrene dihydro-  
bromide with quinoline did not yield  
the expected pure carvestrene, but  
yielded a mixture consisting of four  
components of which ( $\pm$ )-sylvestrene,  
isosylvesterpino-  
lene and sylveterpino-  
lene amounted to 35.07, 24.80 and  
37.86% respectively.

### Kinetics of Hydrogen Chemisorption by Elovich Equation

The role of active centres in chemisorp-  
tion through the application of  
Elovich equation for the kinetic  
data on H<sub>2</sub>/nickel-magnesia and  
H<sub>2</sub>/nickel-alumina systems has been  
elucidated by Yeddanapalli *et al.*

In continuation of these studies,  
the application of the Elovich equa-  
tion for evaluating the apparent  
activation energies with a view to  
accounting for the temperature ano-  
maly of the activation energies was  
investigated. The investigation was  
carried out by Shri P. Samuel, a  
CSIR research fellow, at the Depart-  
ment of Chemistry, Loyola College,  
Madras, under the guidance of Rev.  
Prof. L. M. Yeddanapalli.

The kinetics of hydrogen chemi-  
sorption on different catalysts con-  
taining molybdenum in the form of  
mixed sulphides, disulphides on alu-  
mina, and coprecipitated and im-  
pregnated oxides of molybdenum on  
alumina and on reduced molybdena-  
alumina samples was studied using  
the conventional BET apparatus and  
the constant volume adsorption  
method. The effect of temperature  
and pressure (both initial and am-  
bient) on the kinetics, the effect of  
preadsorbed oxygen and hydrogen on  
the kinetics as well as the effect of  
various methods of preactivation  
were the other aspects studied. Ana-  
lysis of the results was carried out

using Elovich equation,  $dq/dt = a \exp(-\alpha q)$ , where  $a$  and  $\alpha$  are constants  
and  $q$  is the amount of gas adsorbed  
at time  $t$ . The constants were evalua-  
ted by a statistical procedure due to  
Allen and Scaife and certain modifi-  
cations were suggested.

The results show that in a dece-  
lating chemisorption process the  
initial rates describe the process  
better than the conventionally mea-  
sured slow rates (overall). The im-  
portance of the initial surface cover-  
age on the slow kinetics, hither-  
to not considered, has been explained.

Changes in the ambient pressure  
affect the subsequent rates. This  
seems to be more pronounced when  
the changes are made at the initial  
stages than towards the end. The  
coprecipitated catalysts seem to be  
more susceptible to the pressure  
changes than the impregnated cata-  
lysts.

Preactivation with hydrogen  
shows a decrease in the rates of fast  
(initial) and slow (ambient) adsorp-  
tions as revealed by a decrease in  $a$   
and an increase in  $\alpha$ . Preactiva-  
tion with oxygen of the reduced  
molybdena-alumina enhances the  
total amount of hydrogen adsorbed  
by two-fold while the amount of fast  
adsorption as well as the initial rates  
are not very much affected. However,  
the ambient rate increases as the  
adsorption proceeds, thereby indi-  
cating the process to go by a different  
mechanism, presumably through a  
new surface complex developed as a  
result of the promotion of the Mo  
atoms to a higher valence state  
through oxygen bonding. This sur-  
face change seems to be of a perma-  
nent nature as shown by an altogether  
different nature of the  $q$ -log  $t$  plots  
when compared with the normal hy-  
drogen adsorption run as also by the  
fact that even after a prolonged de-  
gassing for more than 15 hr at 420°C  
and at 10<sup>-6</sup> cm, the earlier experi-  
ments could not be reproduced.

Adsorption on the sulphides  
seems to proceed by the Taylor-  
Thon mechanism. The molyb-  
denum atoms with the free  
valences seem to be involved in the  
initial site creation process as re-  
vealed by low activation energies.  
The variation of the Elovich para-  
meters is in excellent agreement  
with the Taylor-Thon observations.  
Taylor-Thon mechanism, however,



## PATENTS

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does not seem to be applicable to the oxides in the low temperature region where molecular adsorption predominates. There seems to be a gradual creation of favourable sites during the induction period for adsorption. Such a process calls for the assumption of an intermediate species accelerating the rate. Recent evidence by ESR suggests the species to be  $\text{Mo}^{5+}$ . The overall process is conceived as molecular adsorption at the initial stages resulting in the formation of a surface complex, and as the  $\text{Mo}^{5+}$  accumulates, the rate proceeds faster by an exponential law. A self-regeneration process involving reduction and re-oxidation of the surface through diffusion has been proposed.

Shri Samuel (presently at the Central Fuel Research Institute, Dhanbad) was awarded the Ph.D. degree (1970) of the Madras University for his thesis entitled 'Chemisorption and catalytic transformations on desulphurization catalysts: Kinetics of  $\text{H}_2$  chemisorption by Elovich equation'.

## Seminar on Electrochemistry

The eleventh seminar on Electrochemistry will be held at the Central Electrochemical Research Institute, Karaikudi from 24 to 27 Nov. 1970. An annual feature of the activities of the institute, the seminar will take stock of the developments that have taken place in the various branches of electrochemistry during the previous year. Papers will be presented in the following seven technical sessions: (1) Batteries; (2) Electro-organic and electro-inorganic products; (3) Electrothermics and electrometallurgy; (4) Electrode kinetics, electrochemical equilibria and electroanalysis; (5) Corrosion; (6) Solid state electrochemistry; and (7) Electrodeposition and metal finishing. Both original and review papers including techno-economic data collected in the operation of electrochemical plants will be accepted for presentation at the seminar. The review papers should, however, be limited to the most recent developments in the fields.

Enquiries regarding the seminar may be addressed to: Dr K. S. Rajagopalan, Convener, Eleventh Seminar on Electrochemistry, Central Electrochemical Research Institute, Karaikudi 3.

125852: An improved electron beam injection system for vacuum devices, G. S. Sidhu & R. P. Wadhwa—CEERI, Pilani.

125853: Process for making oil well cement utilizing shaft kiln plant, S. N. Dutta, T. Seshadri, B. C. Jana, T. C. Saikai & M. S. Iyengar—RRL, Jorhat.

125965: Improvements in or relating to the manufacture of tubular products such as waveguides for microwaves, J. Singh & F. Singh—CEERI, Pilani.

126063: Improvements in or relating to the modification of aluminium base alloys containing silicon, V. A. Altekar, G. C. Nair & P. K. Gupte—NML, Jamshedpur.

126064: Improvements in or relating to wire helix winding for electronic devices such as travelling wave (TWT), Jaswant Singh—CEERI, Pilani.

## ACCEPTED

115086: A process for the production of groundnuts fortified with essential amino acids, K. Narayana, H. A. B. Parpia & P. K. Ramathan—CFTRI, Mysore.

116648: Chlorine tablets, B. N. Pathak & K. R. Bulusu—CPHERI, Nagpur.

116997: Iodine tablets, B. N. Pathak, K. R. Bulusu & S. B. Dabadghao—CPHERI, Nagpur.

118016: Improvements in or relating to electrode holder for the electrochemical marking of metals, S. Guruswamy—CECRI, Karaikudi.

118033: A new process for the production of domestic fuel from coal, M. S. Iyengar, R. K. Chakrabarti, R. Haque, M. L. Dutta & J. Borgohain—RRL, Jorhat.

119756: Process for the manufacture of calcium silicates, H. V. Shah, V. P. Pandya & D. J. Mehta—CSMCRI, Bhavnagar.

120704: Process for the preparation of potassium carbonate and N-K fertilizer using ion-exchange technique, D. R. Baxi & M. C. Modi—CSMCRI, Bhavnagar.

92273: A process for vacuum puffing and dehydration of vegetables, K. E. Eapen & P. K. Ramathan—CFTRI, Mysore.

98146: Development of a process for the manufacture of food beverages, T. K. Ananthachar & B. H. S. Rau—CFTRI, Mysore.

105271: Process for retaining unsaturation during conversion of partially epoxidized glycerides and esters to corresponding monohydroxy compounds, K. T. Achaya & R. Subbarao—RRL, Hyderabad.

107725: A tamping machine, J. P. Kaushish & S. A. Siddiqi—CBRI, Roorkee.

107861: Non-linear discs for use in lightning arrester/surge diverters, M. A. V. Devanathan, V. Rengachari, R. Radhakrishnan, K. S. G. Doss & J. P. Nityanandan—CECRI, Karaikudi.

108145: A device for intra-ovarian injection in large animals, S. N. Chatterjee, K. Ahmad & A. B. Kar—CDRI, Lucknow.

108413: A process for the treatment of costus roots (*Saussurea lappa*) for isolation of inulin, G. H. Kulkarni, G. R. Kelkar, J. L. Bose & S. C. Bhattacharyya—NCL, Poona.

## MEETINGS

The first conference of the Chairmen of the Executive Councils of the national laboratories and industrial research associations and the 18th Conference of the Directors of national laboratories and industrial research associations will be held on 3 and 4 July 1970 respectively at 10.30 a.m. in the Committee Room 'B', Vigyan Bhavan, New Delhi.

The Board of Scientific & Industrial Research (BSIR) and the Governing Body of CSIR will meet on 23 and 24 July 1970 respectively at 10 a.m. in the conference room of the Ministry of External Affairs, South Block, New Delhi. The Technical Committee of BSIR will meet on 22 July 1970 at 10.00 a.m. in the conference room, CSIR, Rafi Marg, New Delhi. The annual general meeting of the Society will be held immediately after the meeting of the Governing Body on 24 July 1970.